ORIGINAL PAPERS

INCLUSIONS AND FERRITE CRYSTALLIZATION IN STEEL[1]

By Edward G. Mahin

The injurious effects exerted by non-metallic inclusions upon the properties of iron and steel have long been recognized but no attempt to avoid the presence of such inclusions has been entirely successful. Their origin may be outlined briefly.

1—During the process of slag formation in the furnace the agitation of liquid iron results in trapping minute particles of slag, whose relative surface is so large as to prevent rapid separation. Many of these remain with the iron when it is tapped from the furnace and they are finally definitely locked up in the solidified ingot.

2—Manganese is added to steel in order to correct the objectionable effects of sulfur and to add desirable properties of its own. Manganese sulfide then forms distinct small particles, recognizable under the microscope as pale gray, rounded or elongated masses. They may contain also certain variable quantities of ferrous sulfide or of manganese.

3—During passage of the melted steel to the moulds oxidation of manganese sulfide occurs, manganese oxide and sulfur dioxide being produced, the latter escaping. At the same time there is some oxidation of iron silicide, ferrous oxide and silicon dioxide being formed. The result of the proximity of these bodies is the formation of a secondary slag, consisting of one or more of the silicates of iron and manganese, or mixtures or solutions of these with each other or with manganese sulfide.[2]

These processes give rise to the formation of rather complex materials and the recognition of distinct compounds becomes very difficult. Ordinary methods of chemical analysis are entirely useless for the purpose because the particles are usually so minute as to make a separation into their physical components impossible. Qualitative tests, together with metallographic and other examination of artificially produced inclusions of known composition, have made possible the following approximate statements:

1—The pale gray rounded or elongated masses, occurring either alone or embedded in a darker matrix, are manganese sulfide, possibly containing dissolved ferrous sulfide or manganese.

2—Darker gray masses, sometimes of varying shading and often carrying lighter masses of manganese sulfide or of silicates of different composition, are one or more of the silicates $FeO.SiO_2$, $2FeO.SiO_2$, $MnO.SiO_2$, $2MnO.SiO_2$, or solid solutions of these in each other. Figs. 1 and 2 illustrate these forms of inclusions.

The effects of inclusions upon the properties of steel may be regarded as being essentially the same as would be produced by cavities of similar size and shape. Many failures of steel have been traced to inclusions. For instance, Fay[1] has shown that a large number of failures of steel rails are due to manganese sulfide inclusions occurring in abnormal quantities. In addition to this easily understandable effect there has long been noticed a certain connection between inclusions and grain formation that has been the subject of much discussion. Ordinary annealed steel of hypo-eutectoid composition is usually found to contain practically all of the inclusions within ferrite grains, and very rarely in pearlite.

Whatever may be the real cause of this phenomenon the result is the segregation of ferrite about the inclusions, often in relatively large granules or thickened network, this structure taking the place of the more nearly normal dissemination of smaller grains. Figs. 3 and 4 illustrate the structure of a steel containing manganese sulfide in ferrite. In these figures and in Fig. 5 some of the inclusions are indicated by arrows. Similar inclusions will be recognized without difficulty in the other photomicrographs. When a steel having such a structure is rolled or forged all structural entities are flattened or elongated and the result is a banded structure appearing in the section as alternating streaks of pearlite and ferrite with the latter containing the inclusions, now in the form of plates, threads, or elongated particles, according to the nature of the working that has been performed. Streaks thus appearing in section are often called ferrite "ghosts."

Segregation which has occurred in steel containing inclusions cannot be corrected by any ordinary thermal treatment, such as would break up ordinary grain systems and generate new ones. The steel is left in practically the same condition as before the treatment, except that grain size may be changed according to the time consumed and the temperature attained by the thermal treatment. If the steel is one that has not been subjected to mechanical treatment the inclusions will still be found within ferrite grains, whether the latter be large or small. If the steel has been previously rolled or forged the banded structure will persist through many repetitions of the reheating process and the threads of inclusions will still be found in the ferrite bands.

Whether the presence of non-metallic inclusions is the *cause* of ferrite segregation or simply incidental to it is a question that has been the subject of considerable interesting experimentation and discussion. Brearley suggested that inclusions are the cause of ferrite segregation and Ziegler proposed[2] as an explanation of the co-segregation of ferrite and inclusions the view that at high temperatures the inclusions are present as a more or less homogeneous solid solution in austenite and that as the latter begins to form grains at temperatures somewhat higher than Ar_3 the impurities are rejected to the grain boundaries where they serve, at Ar_3, as nuclei for the crystallization of ferrite. Ziegler's theory has never been generally accepted, as there is a mass of experimental evidence against it, as well as serious theoretical objections.

[1] Presented before the Indiana Section on January 17, 1919, and before the Division of Chemists and Chemical Engineers of the American Chemical Society at the Buffalo Meeting, April 7 to 11, 1919.

[2] McCance, *J. Iron and Steel Inst.*, **97** (1918), 256.

[1] *Proc. Am. Soc. Testing Materials*, **8** (1908), 74.

[2] *Rev. métall.*, **8** (1911), 655.

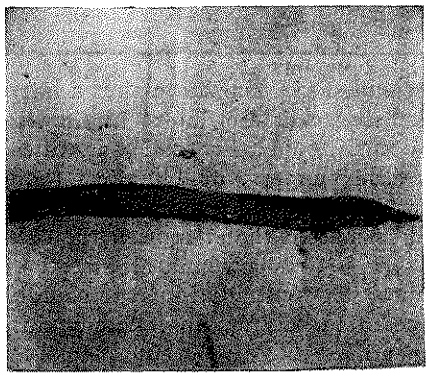

FIG. 1—SLAG FIBER IN ROLLED STEEL. × 500

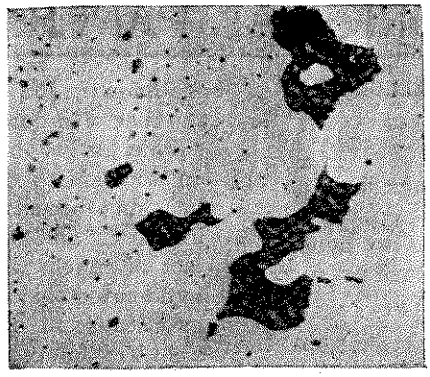

FIG. 2—SLAG IN WROUGHT IRON. × 100

FIG. 3—STEEL. INCLUSIONS SURROUNDED BY FERRITE. × 500

FIG. 4—STEEL. INCLUSIONS SURROUNDED BY FERRITE. × 500

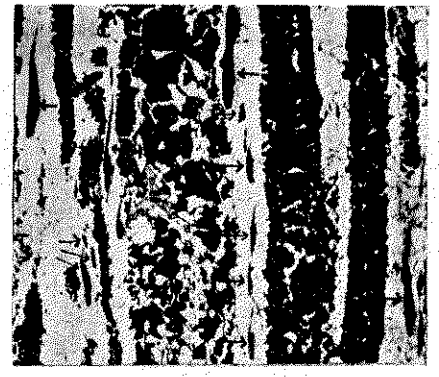

FIG. 5—UNTREATED RAIL ETCHED WITH NITRIC ACID. ELONGATED INCLUSIONS (DARK) LYING WITHIN FERRITE BANDS (LIGHT). × 100

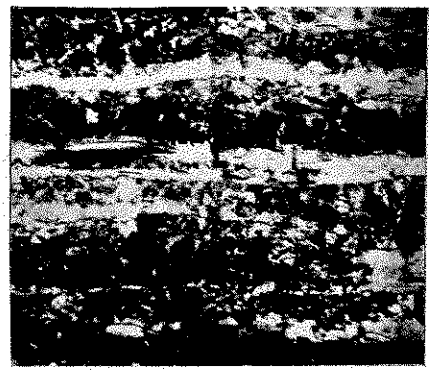

FIG. 6—UNTREATED RAIL ATTACKED BY COPPER REAGENT. × 100

FIG. 7—STEEL HELD AT 850° TO 1000° FOR 91 HRS. ETCHED WITH NITRIC ACID. × 100

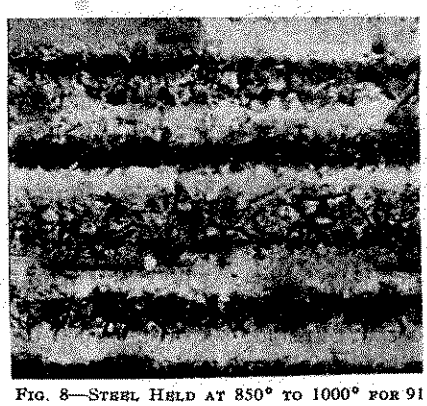

FIG. 8—STEEL HELD AT 850° TO 1000° FOR 91 HRS. TREATED WITH COPPER REAGENT. × 100

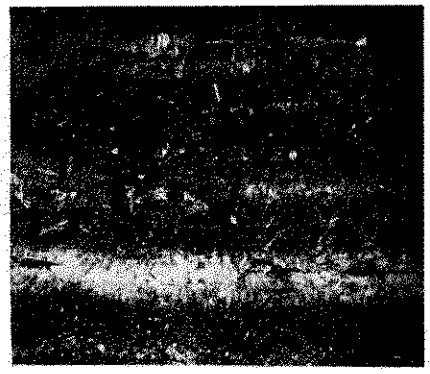

FIG. 9—STEEL QUENCHED IN OIL AT 20°. ETCHED WITH NITRIC ACID. × 100

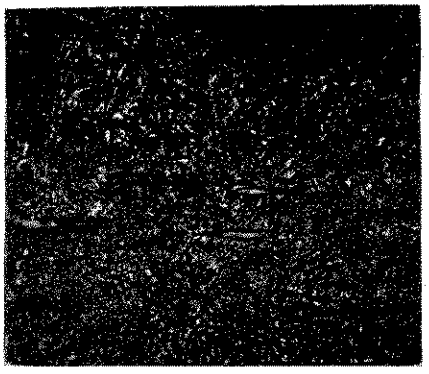

FIG. 10—STEEL QUENCHED IN WATER AT 20°. ETCHED WITH NITRIC ACID. × 100

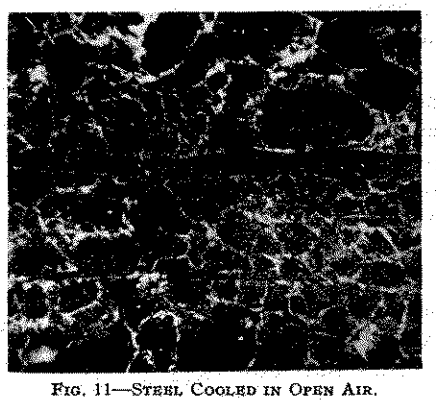

FIG. 11—STEEL COOLED IN OPEN AIR. ETCHED WITH NITRIC ACID. × 100

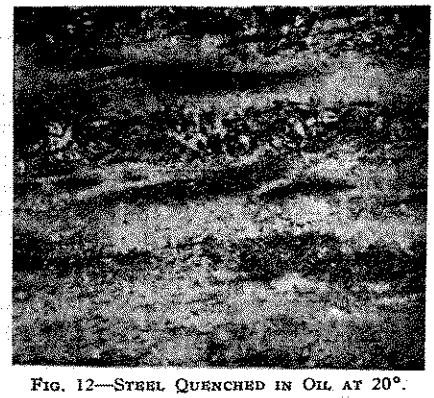

FIG. 12—STEEL QUENCHED IN OIL AT 20°. TREATED WITH COPPER REAGENT. × 100

FIG. 13—STEEL QUENCHED IN WATER AT 20°. TREATED WITH COPPER REAGENT. × 100

FIG. 14—STEEL COOLED IN OPEN AIR. TREATED WITH COPPER REAGENT. × 100

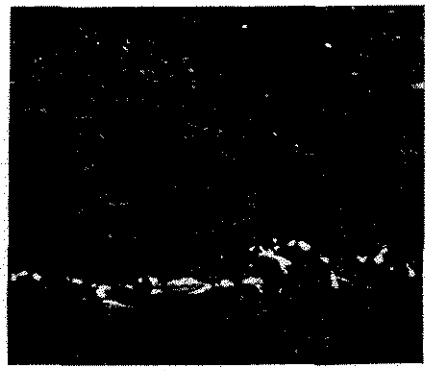

FIG. 15—STEEL COOLED IN FURNACE TO 775°, THEN QUENCHED. ETCHED WITH NITRIC ACID. × 100

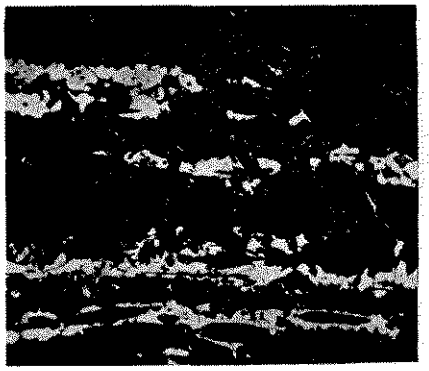

FIG. 16—STEEL COOLED IN FURNACE TO 750°, THEN QUENCHED. ETCHED WITH NITRIC ACID. × 100

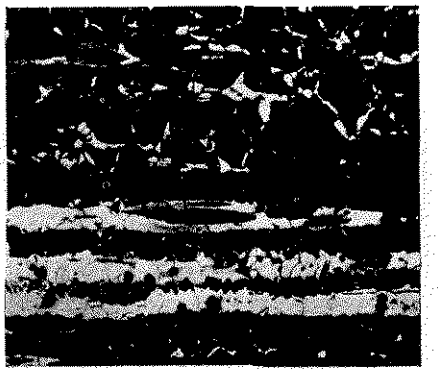

FIG. 17—STEEL COOLED IN FURNACE TO 725°, THEN QUENCHED. ETCHED WITH NITRIC ACID. × 100

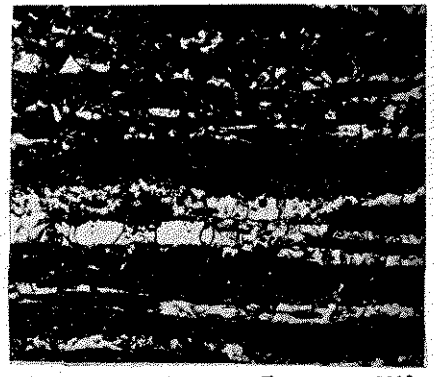

FIG. 18—STEEL COOLED IN FURNACE TO 700°, THEN QUENCHED. ETCHED WITH NITRIC ACID. × 100

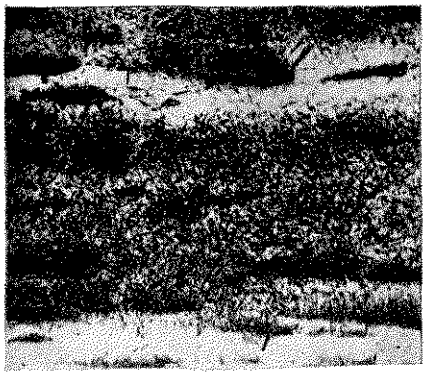

FIG. 19—STEEL COOLED IN FURNACE TO 775°, THEN QUENCHED. TREATED WITH COPPER REAGENT. × 100

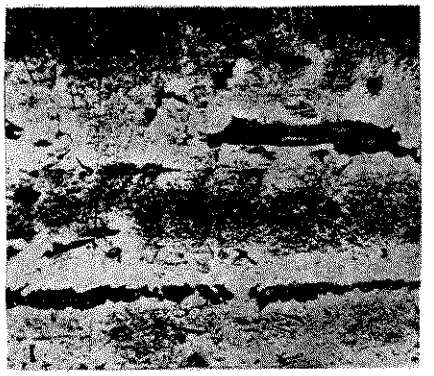

FIG. 20—STEEL COOLED IN FURNACE TO 750°, THEN QUENCHED. TREATED WITH COPPER REAGENT. × 100

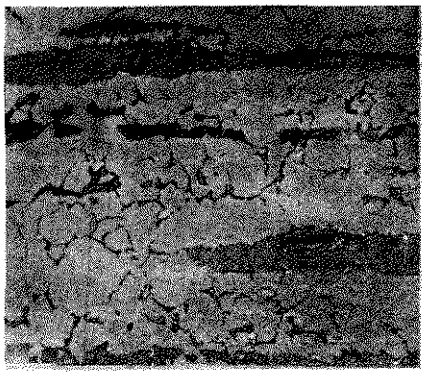

FIG. 21—STEEL COOLED IN FURNACE TO 725° THEN QUENCHED. TREATED WITH COPPER REAGENT. × 100

FIG. 22—STEEL COOLED IN FURNACE TO 700°, THEN QUENCHED. TREATED WITH COPPER REAGENT. × 100

FIG. 23—STEEL HEATED FOR 3 DAYS AT 1100°. ETCHED WITH NITRIC ACID. × 100

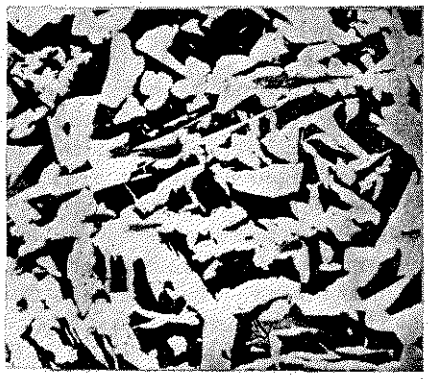

FIG. 24—STEEL HEATED FOR 3 DAYS AT 1100° ETCHED WITH NITRIC ACID. × 100

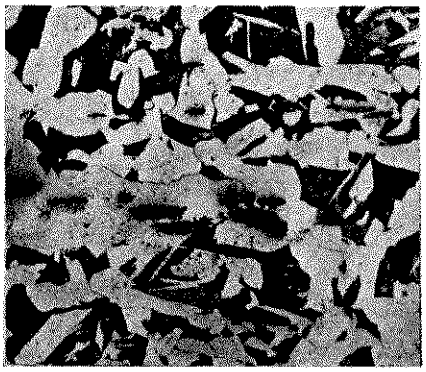

FIG. 25—STEEL HEATED FOR 3 DAYS AT 1100°. ETCHED WITH NITRIC ACID. × 100

FIG. 26—STEEL HEATED FOR 3 DAYS AT 1100°. TRANSVERSE SECTION. ETCHED WITH NITRIC ACID. × 500

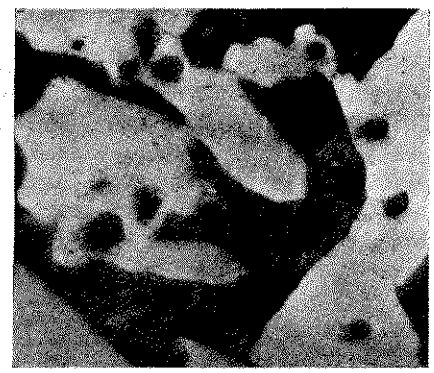

FIG. 27—STEEL HEATED FOR 3 DAYS AT 1100° TRANSVERSE SECTION. ETCHED WITH NITRIC ACID. × 500

FIG. 28—STEEL HEATED FOR 3 DAYS AT 1100°. TRANSVERSE SECTION. ETCHED WITH NITRIC ACID. × 500

FIG. 29—STEEL HEATED FOR 3 DAYS AT 1100°. TRANSVERSE SECTION. ETCHED WITH NITRIC ACID. × 500

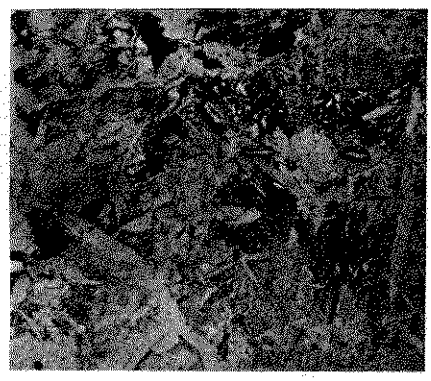

FIG. 30—STEEL HEATED FOR 3 DAYS AT 1100° LONGITUDINAL SECTION. TREATED WITH COPPER REAGENT. × 100

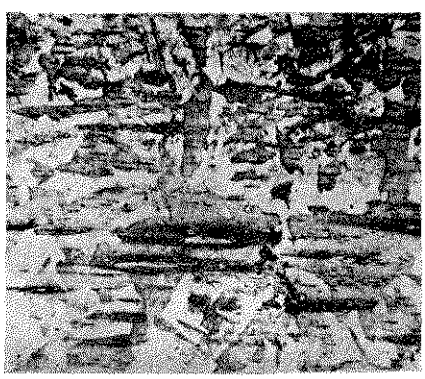

FIG. 31—STEEL HEATED FOR 3 DAYS AT 1100°. LONGITUDINAL SECTION. TREATED WITH COPPER REAGENT. × 100

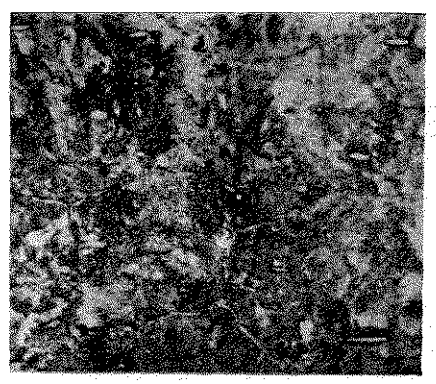

FIG. 32—STEEL HEATED FOR 3 DAYS AT 1100°. LONGITUDINAL SECTION. TREATED WITH COPPER REAGENT. × 100

FIG. 33—STEEL HEATED FOR 3 DAYS AT 1100°. TRANSVERSE SECTION. TREATED WITH COPPER REAGENT. × 100

This theory would involve the reabsorption of inclusions when steel is reheated to temperatures considerably above Ac_3, a supposition that is absolutely without experimental justification. It will be shown later in the present paper that elongated inclusions in rolled steel retain their form and orientation even after prolonged heating at 1100°, a fact which would not be noticed if absorption and coagulation had successively taken place. Similar observations have been made by numerous other investigators.

Quite otherwise has been the reception of the idea that inclusions can act repeatedly as nuclei for crystallization of ferrite as the latter is thrown out of solid solution during the cooling of austenite through the transformation range. This view has been accepted by many metallurgists, although combatted vigorously by others, notably Stead and H. M. Howe. The former has carried on investigations regarding the relations existing between phosphorus and iron, as one result of which he concludes that slag or other inclusions are not, in any sense, the direct cause of ferrite segregation but that they are purely incidental to it. He has brought out, by very extensive experiments, the behavior of iron phosphide in both high and low phosphorus steel and its effect upon carbon distribution.[1] However, it may fairly be doubted whether the matter is settled, so far as the general acceptance of his views regarding inclusions is concerned. Briefly, Stead's theory is as follows:

The "solid solution pressure" of iron phosphide

[1] *J. Iron and Steel Inst.*, **58** (1900), 60; **91** (1915), 140; **97** (1918), 287 and 389.

and iron carbide existing together in austenite is greater than that of iron carbide alone. When a steel containing phosphorus cools, these two substances therefore tend to withdraw from each other and, as carbide is more mobile than phosphide, the result is concentration of carbide in localities relatively free from phosphide. Thus steel cooling past Ar_3 becomes supersaturated with ferrite earliest in the phosphoretic regions and ferrite accordingly separates first at these points. The insoluble inclusions are also found in the regions high in phosphorus because cooling of liquid steel leaves iron phosphide and inclusions in the last portions to solidify. It is then concluded (1) that phosphorus and inclusions generally occur together and (2) that carbon recedes from phosphorus during cooling through the transformation range, leaving ferrite containing dissolved iron phosphide surrounding the inclusions. Stead thus regards phosphorus as being the true cause of segregation of this kind.

Howe[1] also expresses the idea that the occurrence of inclusions within ferrite (or cementite) grains or network is due to the tendency of austenite to reject both inclusions and ferrite to grain boundaries during the process of crystal formation and when cooling through the transformation range. Theoretical reasoning and experimental evidence are brought forward in support of this view and Howe also shows that the logical result of this action is expulsion of ferrite and inclusions to the surface of the piece, thus giving a low-carbon and highly impure surface layer. Ferrite segregation is shown to exist in the zone immediately surrounding mechanical cavities in steel.

In the course of Stead's paper on "Inclusions in Steel and Ferrite Lines,"[2] he reports a series of experiments designed to test the question as to whether non-metallic inclusions or mechanically produced cavities induce the crystallization of ferrite about them. In these experiments small holes were drilled in three series of hypo-eutectoid steels. Some of these holes were then partly filled with various powdered materials while others were left empty. The holes were tightly plugged and the plugs were sealed in. The pieces were heated to high temperatures and some were reheated to 1000° C. and cooled slowly. The substances used as inclusions were quartz, magnesia, fluorspar, lime, basic slag, titanium cyanonitride, acid slag, mill scale, and manganese sulfide. The polished and etched sections failed to exhibit any evidence of ferrite segregation at the borders of the inclusions, with the single exception of fluorspar. From this it is concluded that neither inclusions of the sort usually found in steel nor cavities themselves can act as nuclei for ferrite crystallization.

It is difficult to see how these experiments can be regarded as conclusive. No matter how finely the materials might be powdered or how closely packed, a certain (though small) amount of air would necessarily be enclosed in the interstices between the powder grains. Upon heating the piece the very first effect would be to produce a film of oxide upon the lining of the cavity. This must necessarily prevent the close and intimate contact that occurs between steel and inclusions when these have cooled from the liquid state together, and for this reason it would appear that inclusions produced in this manner could exert little or no effect upon carbon segregation, although they might act as would cavities of corresponding size.

[1] "The Metallography of Steel and Cast Iron," pp. 280, *et seq.*

[2] *J. Iron and Steel Inst.*, **97** (1918), 287.

EXPERIMENTAL

A section of an open hearth steel rail was selected, having the following composition: Carbon 0.55, silicon 0.06, phosphorus 0.14, sulfur 0.13, manganese 0.85. From such a statement one might expect to find comparatively small amounts of siliceous slag but appreciable quantities of manganese sulfide. This rail exhibited a pronounced banded structure, ferrite streaks almost without exception containing threads and elongated particles of inclusions. The structure of the untreated material is shown in Fig. 5, etched with nitric acid, and in Fig. 6, treated with Stead's copper reagent.[1] The dark areas in Fig. 6 show where copper has coated iron that is relatively free from phosphorus, while the light areas are higher in phosphorus.

FIRST SERIES—Four pieces of this material were placed in a furnace and held at temperatures ranging from 850° to 1000° C. The furnace was cooled after periods of 18, 41, 67, and 91 hrs., respectively, one piece being removed after each period. Fig. 7 shows that this treatment served to break up the continuity of pearlite bands to a considerable extent and to coarsen the grain, but that the inclusions are not changed in form and that they still lie surrounded by ferrite. Fig. 8 shows the action of Stead's copper reagent upon the material that had been heated for 91 hrs. Phosphide bands are still shown in a very striking manner and it is interesting here to note that inclusions do lie, for the most part, in the phosphide bands. That this rule is not without many exceptions will be made clear presently.

SECOND SERIES—One each of five specimens was heated to 900° C. and quenched. The quenching media were as follows: Oil at 20°, water at 20°, iced brine at approximately —10°, water at 100°, and open air. Figs. 9 and 10 illustrate some of the structures as brought out by etching in nitric acid. The specimens that were quenched in oil or water are sorbitic or martensitic. There is little evidence of carbon segregation except in the specimen quenched in oil. Here ferrite bands begin to appear and inclusions are found in these bands. The specimen that was air cooled has been caught at the beginning of ferrite formation and the normal arrangement of ferrite network surrounding sorbitic grains is evident. (The slag thread that is seen in this photomicrograph is abnormally large and is, in this respect, not representative.)

These photomicrographs show that above Ar_3 the carbon distribution is uniform, so far as the microscope is able to detect, and that when cooling is moderately

[1] Cupric chloride, 1 g.; magnesium chloride, 4 g.; hydrochloric acid, 1 cc.; water, 20 cc.; absolute alcohol, 100 cc. This reagent deposits copper upon the areas lowest in phosphorus.

rapid, as in air quenching, ferrite is rejected at the boundaries of austenite grains in a normal manner. We should thus conclude that segregation of ferrite and pearlite into bands requires more time than is allowed by most quenching baths or even by air when the pieces of steel are small. In the case of the air-cooled specimen one may easily notice that a ferrite lining surrounds a considerable part of the threads of inclusions. Figs. 12, 13 and 14 show the action of the copper reagent upon these specimens. Phosphide bands have persisted throughout the treatment and as these are shown to be considerably wider than the inclusions it seems scarcely probable that phosphorus is responsible for the thin ferrite lines lying directly against the inclusion threads in the air-cooled specimen. Attention is also called to the fact that Fig. 14 shows inclusions lying in bands low in phosphorus as well as in those high in phosphorus.

THIRD SERIES—A third series of four specimens was heated to 900° C. and allowed to cool in the furnace to specified temperatures, followed by quenching in iced brine at —10°. The quenching temperatures were 775°, 750°, 725°, and 700° C. In this way an attempt was made to arrest the breakdown of austenite at various stages in order to obtain some information as to the mode of progress of ferrite segregation. Photomicrographs of these specimens are shown in Figs. 15, 16, 17, and 18, as etched with nitric acid, and in Figs. 19, 20, 21, and 22 as acted upon by the copper reagent.

The progress of the changes occurring during cooling may be followed fairly well by this process. Given sufficient time for ferrite and carbide migration, as in furnace cooling, small ferrite grains begin to form around inclusions (Fig. 15). Fig. 19 shows that in the specimen quenched from 775°, inclusions lie in phosphide bands and purer iron bands, almost indiscriminately. In the specimen quenched from 750° (Fig. 16), ferrite bands are wider and considerably more numerous and the rule here, as in other cases, is that inclusions are surrounded by ferrite. Specimens quenched from 725° and 700° (Figs. 17 and 18) show further progress of these changes, although the austenite is not completely broken down, even at the latter temperature.

The action of the copper reagent upon the pieces quenched from 750°, 725°, and 700°, respectively, is worthy of special notice. It is rather remarkable that, in these cases, inclusions that lie in phosphorus-rich bands are, nevertheless, surrounded by well-defined zones of purer iron, comparatively free from phosphorus. This is very strikingly shown in Figs. 20, 21, and 22. Ferrite appears to show, in these specimens, a preference for crystallization about inclusions, leaving not only the solution with iron carbide, but the solution with iron phosphide, as well.

FOURTH SERIES—Stead has shown that long heating at high temperatures will destroy a banded structure and that phosphorus becomes, by this treatment, uniformly distributed. In order to determine what effect this might have upon ferrite segregation, a piece of steel similar to that used in the experiments already described was placed in an iron crucible, covered with fusible glass to prevent oxidation, and heated for three days at 1100° C. After cooling in the furnace the piece was cut for both longitudinal and transverse sections. The results of the nitric acid etching of the longitudinal sections are shown in Figs. 23, 24, and 25, and of transverse sections in Figs. 26, 27, 28, and 29, the last four being at a magnification of 500 diameters. The action of the copper reagent is shown in Figs. 30, 31, and 32 for longitudinal sections and in Fig. 33 for the transverse section. These tests show (1) that all banding, of either ferrite or phosphide, has disappeared as a result of the thermal treatment, (2) that ferrite still persistently crystallizes about inclusions, and (3) that the distribution and orientation of these inclusions has not been altered in any manner.

SUMMARY AND CONCLUSIONS

The writer is unable to confirm Stead's theory, which is to the effect that inclusions are not responsible in any way for ferrite segregation and that such segregation is entirely due to the presence of iron phosphide dissolved in the regions surrounding the inclusions. Neither does Howe's explanation appear to cover the case, in view of the fact that the orientation and relative positions of inclusions appear to remain unaltered by repeated heating and cooling through the transformation range, and by protracted heating at 1100°, followed by slow cooling.

That the *persistence* of ferrite-pearlite banding of forged steel through ordinary thermal treatments is due in considerable measure to the presence of phosphide banding seems to be indicated by the experiments described in this paper, as well as by the work of Stead. If, then, it be granted that certain inclusions may exert some sort of influence upon the segregation of ferrite there still remains the question as to why ferrite ghosts disappear after prolonged heating at high temperatures, since the inclusions remain throughout in their original positions, no migration being observable. It is well here to recall the fact that even in such low-phosphorus steels as this the inclusions are relatively quite small, compared with portions occupied by phosphorus. Forging the mass in such a manner as to produce an approximate cylinder from an approximate sphere elongates the masses in proportion to their respective radii *for a given reduction*, that is, the volume of a sphere is $\frac{4}{3}\pi R^3$ and that of a cylinder is $\pi r^2 l$, where R and r represent the radii of sphere and cylinder, respectively. For a given reduction $R = ar$, a being a constant for this reduction. Then $l = \frac{4}{3}a^3 r$. For instance, if forging has reduced the radius three times, then $a = 3$ and $l = 36r$, a very considerable attenuation. The inclusion may be regarded as being elongated according to the same law but as its radius is so much shorter than that of the ferrite streak, the absolute difference in the lengths of the two is very large. Measurement of the dimensions of a considerable number of ferrite bands and of the inclusions enveloped by them, in the specimens used in these

experiments, gave an approximate average of 10 for the ratio of the radius of the ferrite band to that of the inclusion. In such a case the distance between the ends of the ferrite cylinder and the corresponding ends of the contained inclusion would be ten times as great as that between the sides of these entities. This would place the major part of a given ferrite streak entirely outside the "sphere of influence" of the inclusion at its core.

The mathematical reasoning given above must be regarded as the roughest sort of approximation for the practical case. The amount of reduction by forging or rolling varies from piece to piece and this does not really produce a cylinder from the original equiaxed grain, but rather a lenticular mass of variable and more or less indefinite form. However, the general qualitative deductions are valid and it is obvious from this that the continued recurrence of ferrite ghosts after repeated cooling through the transformation range must rest upon some action other than the influence of inclusions upon ferrite crystallization, unless the inclusions are scattered fairly thickly and uniformly throughout the recurrent band, a condition that is met in a comparatively small number of cases. The experimental work described in this paper shows that it is only in these exceptional cases that a ferrite band of appreciable length and continuity survives long soaking at 1100° C. and that the long, well-formed bands disappear when iron phosphide has diffused to a fairly uniform distribution throughout the piece. But even after this condition has been reached the large majority of inclusions are still seen to be surrounded by ferrite and, while an occasional particle is seen to penetrate a pearlite grain or even to be embedded in the latter, these cases are exceptional. On the other hand, many instances are shown in the photomicrographs where inclusions are found within pearlite grains *but entirely surrounded* by "islands" of ferrite. A ferrite grain embedded in one of pearlite is not a normal formation and it seems probable that non-metallic inclusions must be found somewhere within most ferrite masses included in this way in pearlite grains, even when the non-metallic inclusion fails to show in the section, since the chance of cutting the relatively small inclusion is so much less than that for the ferrite and pearlite masses.

The work described in this paper would appear to justify the following conclusions:

1—The recurrence of ferrite ghosts after repeated thermal treatment which would serve to break up any ordinary carbon segregation is due, largely if not entirely, to phosphorus banding which is little changed by ordinary treatment.

2—Even after phosphorus distribution has been made uniform, repeated heating followed by slow cooling still leaves inclusions surrounded by ferrite.

The explanation of the second point is not obvious. It might be supposed, as has been held by Brearley, Ziegler, and many others, that the inclusions can act as actual nuclei for crystallization; or it is possible that either the inclusion itself or some reaction product may exist in very dilute solution in a limited zone surrounding the particle and that the solubility of iron in austenite in this zone is thereby lowered in some degree. This would serve to start ferrite separation in these regions, during the cooling process, before supersaturation is ready to break down at other points, with the result that has been seen.

In connection with the hypothesis that the inclusion may act as a crystal nucleus, Rosenhain observed,[1] in the discussion of Stead's paper, that in order that this may be the case the nucleus must itself be isomorphous with the surrounding material. While little appears to be known regarding the crystalline nature of inclusions, reference may be made to Levy's statement[2] to the effect that manganese sulfide crystallizes in the cubic system and to the well-known fact that naturally occurring manganese sulfide (alabandite) also crystallizes in this system. If this should be true the necessary condition is attained for this common inclusion, since alpha iron also crystallizes in the cubic system.

That the materials of inclusions in general are slightly soluble in steel is not to be doubted. Theoretical reasoning would lead to this conclusion and numerous investigators are agreed upon this point. Since the inclusions that are ordinarily regarded as manganese sulfide probably contain also varying (though small) quantities of ferrous sulfide, either of these substances might, conceivably, show the effect mentioned above.[3] That is, by dissolving to a slight extent they might lower the solubility of iron sufficiently to start ferrite separation in the zone surrounding the inclusion before ferrite has been thrown out at other points. No doubt both ferrous sulfide and manganese are present in this zone as equilibrium products of the reaction of manganese sulfide with surrounding iron:

$$MnS + Fe \rightleftarrows Mn + FeS$$

These hypotheses are offered, at this time, merely as suggestions, but some experimental work now in progress will, it is believed, show that the slight solubility of the inclusion in the surrounding metal is actually responsible for the action discussed in this paper. These experiments will be reported in a subsequent paper.

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ANALYTICAL METHOD FOR DETERMINING EFFICIENCY OF AMMONIA OXIDATION

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The writer has read with interest the papers on the analytical control of ammonia oxidation by Fox,[5]

[1] *J. Iron and Steel Inst.*, **97** (1918), 296.

[2] *Carnegie Scholarship Memoirs, Iron and Steel Inst.*, **3** (1911), 304.

[3] It is not considered probable that oxides of iron and manganese can exist in solution in manganese sulfide, in quantities greater than the merest traces. The following reactions would certainly occur at high temperatures:

$$2FeO + MnS \longrightarrow Mn + 2Fe + SO_2$$
$$2MnO + MnS \longrightarrow 3Mn + SO_2$$

[4] Published by permission of the Chief of Ordnance.

[5] THIS JOURNAL, **9** (1917), 737.